Agricultural use of municipal wastewater treatment plant sewage sludge as a source of per- and polyfluoroalkyl substance (PFAS) contamination in the environment

A.B. Lindstrom[1], M.J. Strynar[1], R.L. McMahen[2] L. McMillan[3], D. Knappe[4], E. Arevalo[4], S. Wing[5]

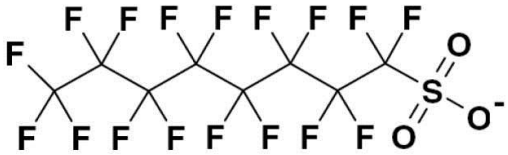
1 U.S. Environmental Protection Agency, National Exposure Research Laboratory, Research Triangle Park, NC
2 Oak Ridge Institute for Science Education, U.S. Environmental Protection Agency, Research Triangle Park, NC
3 National Caucus & Center on Black Aged, Inc., Durham, NC
4 North Carolina State University, Department of Civil, Construction, and Environmental Engineering
5 University of North Carolina, Gillings School of Global Public Health

Third Biosolids Workshop
RMIT University
Melbourne, Australia
September 1, 2015

RMIT UNIVERSITY

Presentation Outline

Discuss per- and polyfluoroalkyl substance (PFAS), their properties, toxicity, and how they get into sewage sludge

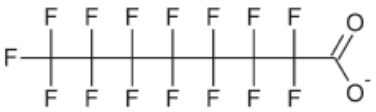


Sewage sludge, regulations and concerns, applications in NC

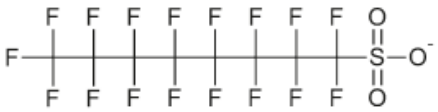
Research showing that sewage sludge from specific waste water treatment plants in NC contains high levels of PFAS - use of sludge as a low cost fertilizer leads to contamination of fields and surface water

Implications regarding the use of sewage sludge

Some per- and polyfluoroalkyl substance (PFAS)

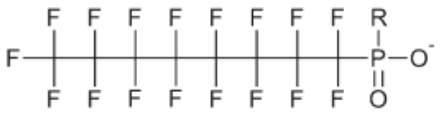


Perfluorocarboxylic acids
(ex. PFOA)

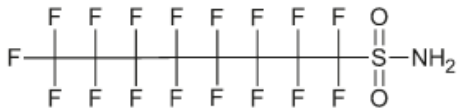


Perfluorosulfonic acids
(ex. PFOS)

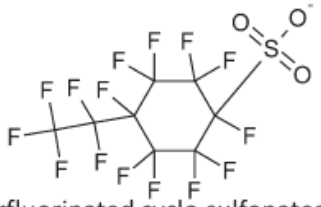
Fluorotelomer alcohol
(ex. 8:2 FTOH)



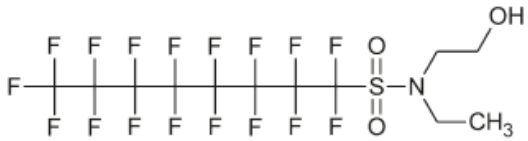
Perfluorophosphonic/phosphinic acids
(ex. If R=OH then PFOPA
If R=C8 perfluoroalkane then 8:8 PFPi)



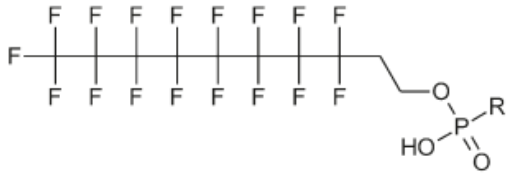
Perfluorosulfonamide
(ex. FOSA)



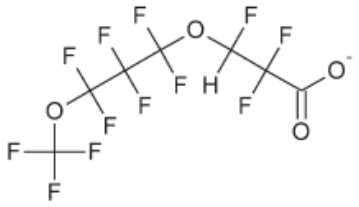
Perfluorinated cyclo sulfonates
(ex. PFECHS)



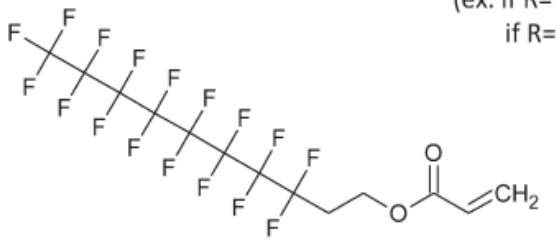
Perfluorosulfonamidoethanol
(ex. N-EtFOSE)



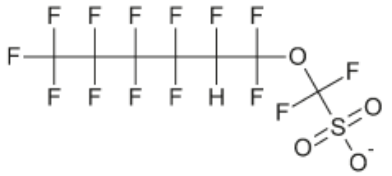
Fluorotelomer phosphate esters
(ex. if R= OH then 8:2 monoPAP
if R= 8:2 FTO ester then 8:2 diPAP)



Polyfluorinated ether carboxylates
(ex. 4,8-dioxa-3H-perfluorononanoate)



Polyfluorinated polymeric unit
(ex. 1H,1H,2H,2H-perfluorodecyl acrylate)



Polyfluorinated ether sulfonates
(ex. Perfluoro [hexyl ethyl ether sulfonate])

Figure 1. Generic structures for polyfluorinated compounds. The $n = 8$ linear carbon structures are shown for many of these examples, but $n = 4-14$ linear and/or branched carbon units are generally possible.

PFAS used in many products

Many PFAS are toxic, extremely persistent, and bioaccumulative

Textile treatments

Paints

Pesticides

Floor polish

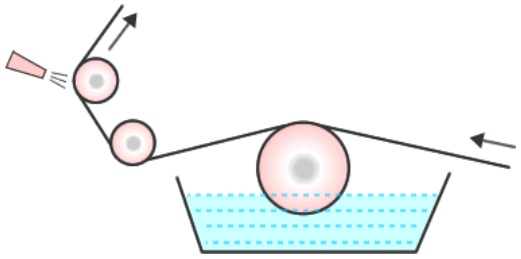
Denture cleaner

Polymers

Adhesives

Lu

Paper coatings



Surfactants

Fire-fighting foam

Photographic film

Shampoo

Non-stick cookware

Caulks

Carpets

Sources of PFAS exposure in humans

Best documented source includes contaminated drinking water around industrial operations e.g., Cottage Grove, Minnesota; Parkersburg, West Virginia; Dalton, Georgia; Decatur, Alabama; Arnsberg, Germany; Osaka, Japan

Food is also implicated in many studies (mostly modeling), but there are few good data on food items (complex matrices). Exception is fish, which is a well documented source.

Fromme et al. 2009, Inter. J. Hyg. & Envr. Heath (212) 239-270

PFAS Health Effects Summary

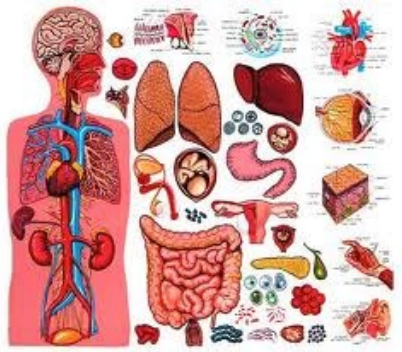
Animal toxicity

- Causes liver, immune system, developmental, endocrine, metabolic, and neurobehavioral toxicity.
- PFOA and PFOS caused tumors in chronic rat studies.

Post et al., (2012) Perfluorooctanoic acid (PFOA) , an emerging drinking water contaminant: A critical review of recent literature, *Environmental Research* (116) 93-117

Human health effects associated with PFAS in the general population and/or communities with contaminated drinking water include:

- ↑ cholesterol
- ↑ uric acid
- ↑ liver enzymes
- ↓ birth weight
- ↓ vaccine response
- Thyroid disease
- Osteoarthritis
- Diabetes
- Testicular and kidney cancer
- Pregnancy-induced hypertension
- Ulcerative colitis
- Effects in young adulthood from prenatal exposures
  - *Obesity in young women.*
  - *↓ sperm count in young men.*



Steenland et al., (2014), *Epidemiology* (25) 167-169; http://www.c8sciencepanel.org/

2009 US Environmental Protection Agency
Short-term Provisional Health Advisories

Provisional Health Advisory levels for PFOS and PFOA in drinking water

PFOS = 200 ng/L PFOA = 400 ng/L

Short term exposure only (months) – no long term (chronic) standard set

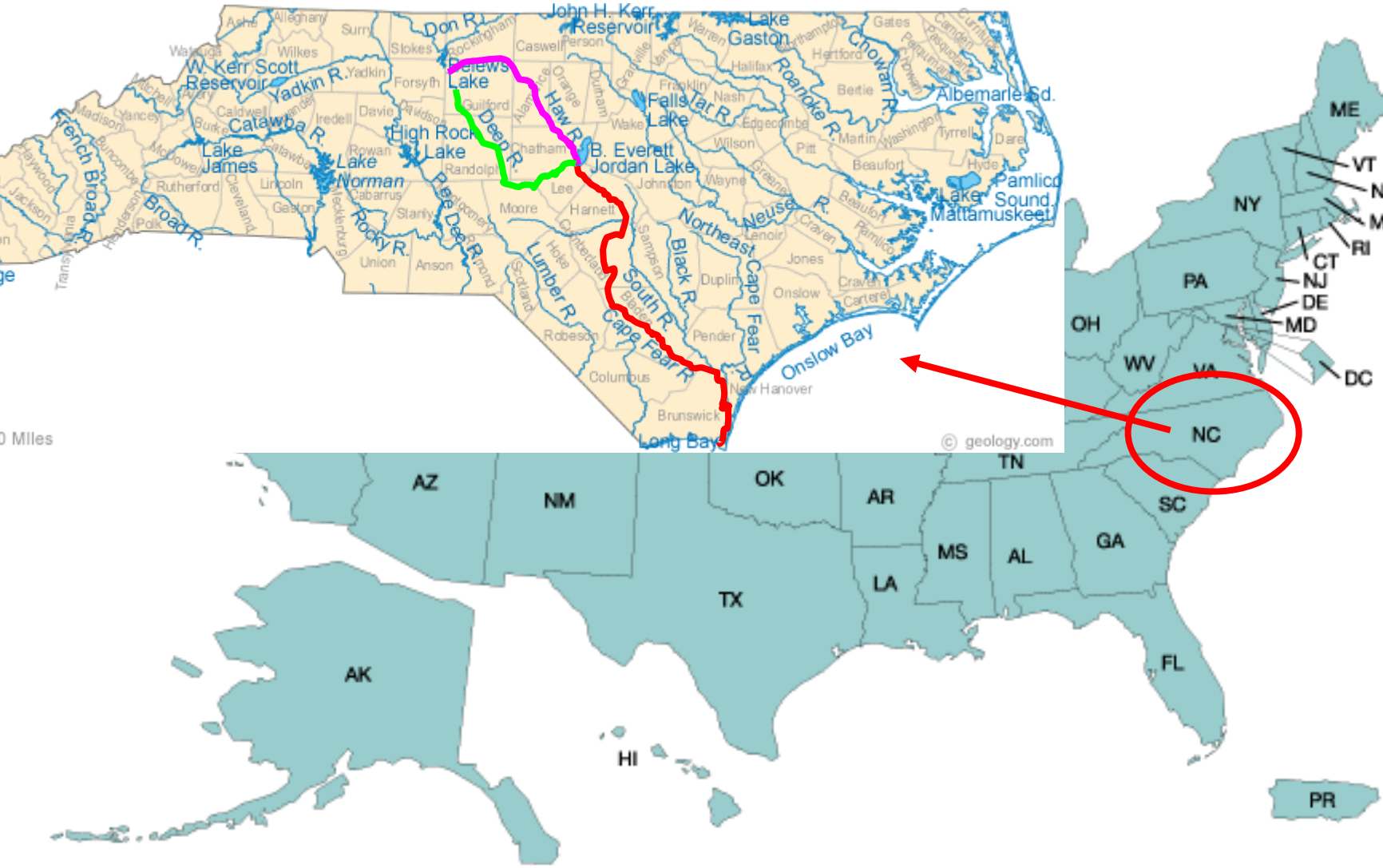
State of New Jersey long-term chronic health-based drinking water guidance for PFOA of 40 ng/L issued in 2007

* Some experts calling for reduction in EPA's Provisional standards by a factor of 100 – 1000 to be truly protective for long-term exposures

PFOS = 2 ng/L PFOA = 4 ng/L

* Immunotoxicity of perfluorinated alkylates: calculation of benchmark doses based on serum concentrations in children Grandjean, P ; Budtz-Jorgensen, E ;Environmental Health (12:35) DOI: 10.1186/1476-069X-12-35, APR 19 2013

The Cape Fear River Basin

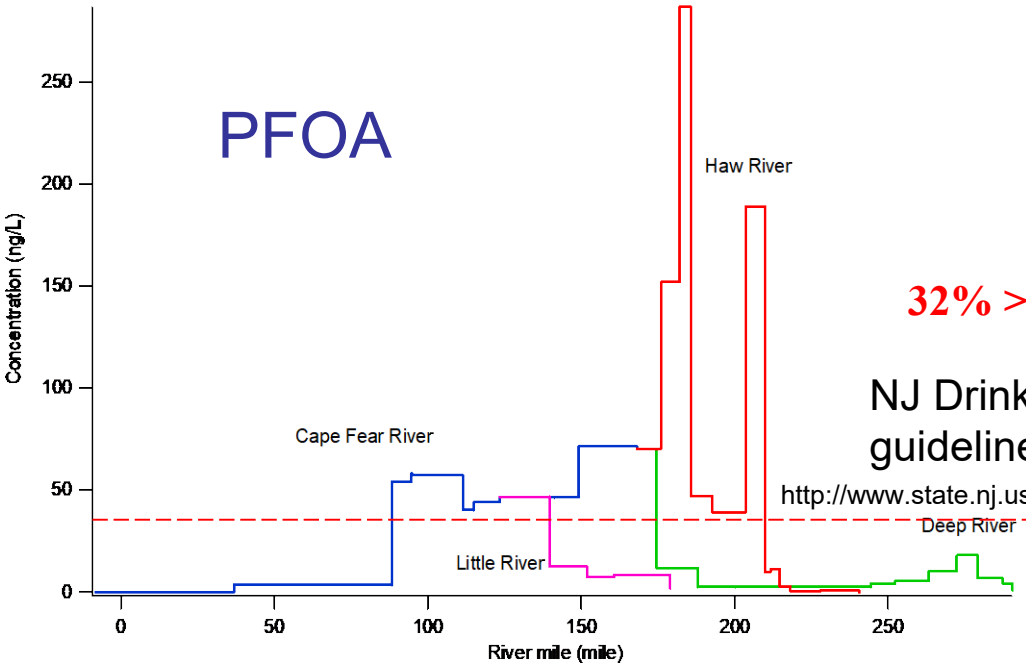


Survey of perfluorinated compounds in surface water 2006

SS Kemmerer sampler

Lab-made dip sampler

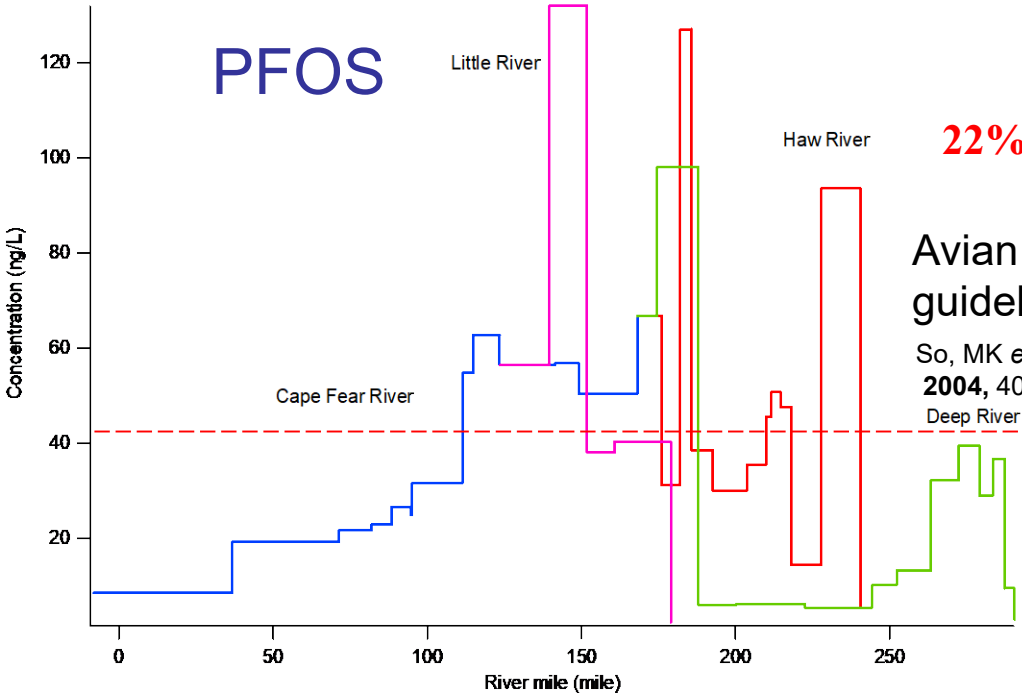
PFC profiles in the Cape Fear Drainage Basin, North Carolina, USA



32% > 40 ng/L

NJ Drinking water guideline 40 ng/L

http://www.state.nj.us/dep/watersupply/pfoa.htm

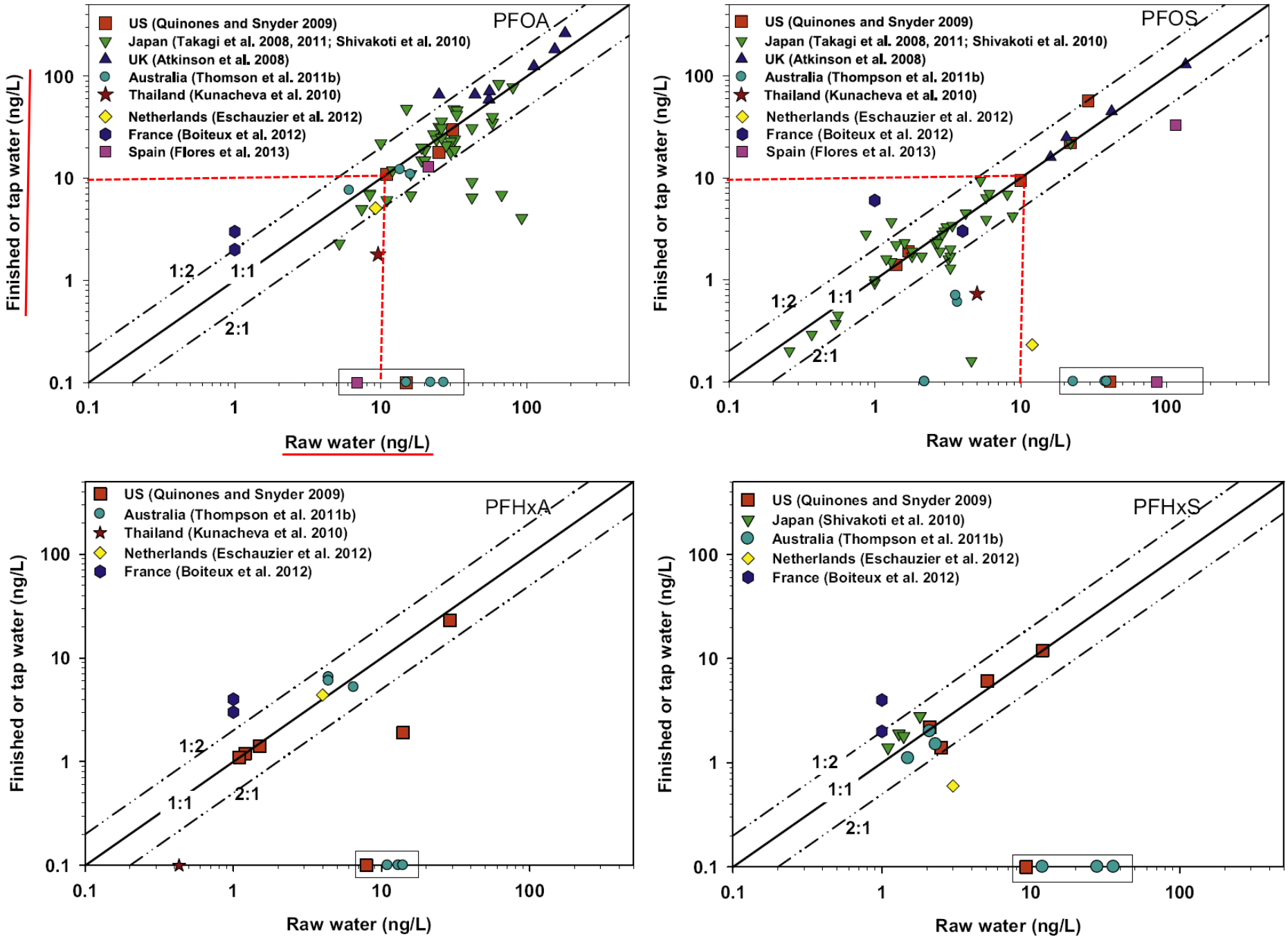


22% > 43 ng/L

Avian wildlife guideline 43 ng/L

So, MK *et al. Environ. Sci. Technol.* **2004,** 4056-4063.

Nakayama *et al. Environ. Sci. Technol.* **2007,** 41: 5271-5276



Rahman et al., (2014) *Water Research,* 50:318-340

Questions

- Why would PFAS concentrations be high and variable in North Carolina?

- Any evidence to suggest that using WWTP sludge as fertilizer leads to elevated PFAS concentrations in North Carolina?

- What are the impacts on communities?

- What are the implications for groundwater and drinking water, livestock, produce, fisheries, etc.?

Documented occurrence of contamination resulting from surface application of sewage sludge:

Moehne River valley in Germany, PFAS contamination of soil, surface water, fisheries resources, agricultural produce, elevated blood levels in humans Skutlarek, D.; Exner, M.; Farber, H. Perfluorinated surfactants in surface and drinking waters. Environ. Sci. Pollut. Res. 2006, 13 (5), 299–307.

Milwaukee, Wisconsin, $4 million remediation effort to remove PCB contaminated "Milorganite" that was applied at 30 municipal parks in the city - contamination exceeding Superfund limits

http://www.jsonline.com/news/milwaukee/29423464.html 2007

Raleigh, North Carolina, $15 million to provide municipal water service residences served by 16 nitrate contaminated wells resulting from excessive applications of sludge

http://www.newhillca.org/wwdocs/RaleighWantsCleanupWaiver.pdf 2007

Decatur, Alabama, PFAS contamination of soil, ground and surface water, fisheries resources, agricultural produce, elevated blood levels in humans

Application of WWTP Biosolids and Resulting Perfluorinated Compound Contamination of Surface and Well Water in Decatur, Alabama, USA: Lindstrom, Strynar, Delinsky; et al. Environmental Science & Technology 2011, 45:19;8015-8021 (and references herein)

Illegal dumping of PCB wastes to Charlotte-Mecklenburg Utilities leads to clean up costs exceeding at least $1.3 million, rural landowners revolt over sludge application

http://www.policyoptions.org/charlotte/article/charlottes-pcb-cleanup-costs-to-top-1-3-million 2014

Three major considerations

Principle of Precaution…"where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost effective measures to prevent environmental degradation". *Commission of the European Communities: (2000)* *http://ec.europa.eu/dgs/health_consumer/library/pub/pub07_en.pdf*

Green Chemistry…always strive to use the least toxic alternative available, with a preference for compounds that quickly and harmlessly degrade to their original starting materials
Anastas PT, Warner JC. 1998. Green Chemistry: Theory and Practice. New York, NY Oxford University Press

Environmental Justice…"the avoidance of hazards and acquisition of benefits through relationships that negatively impact the environment of others" *Steve Wing, (2015) University of North Carolina*

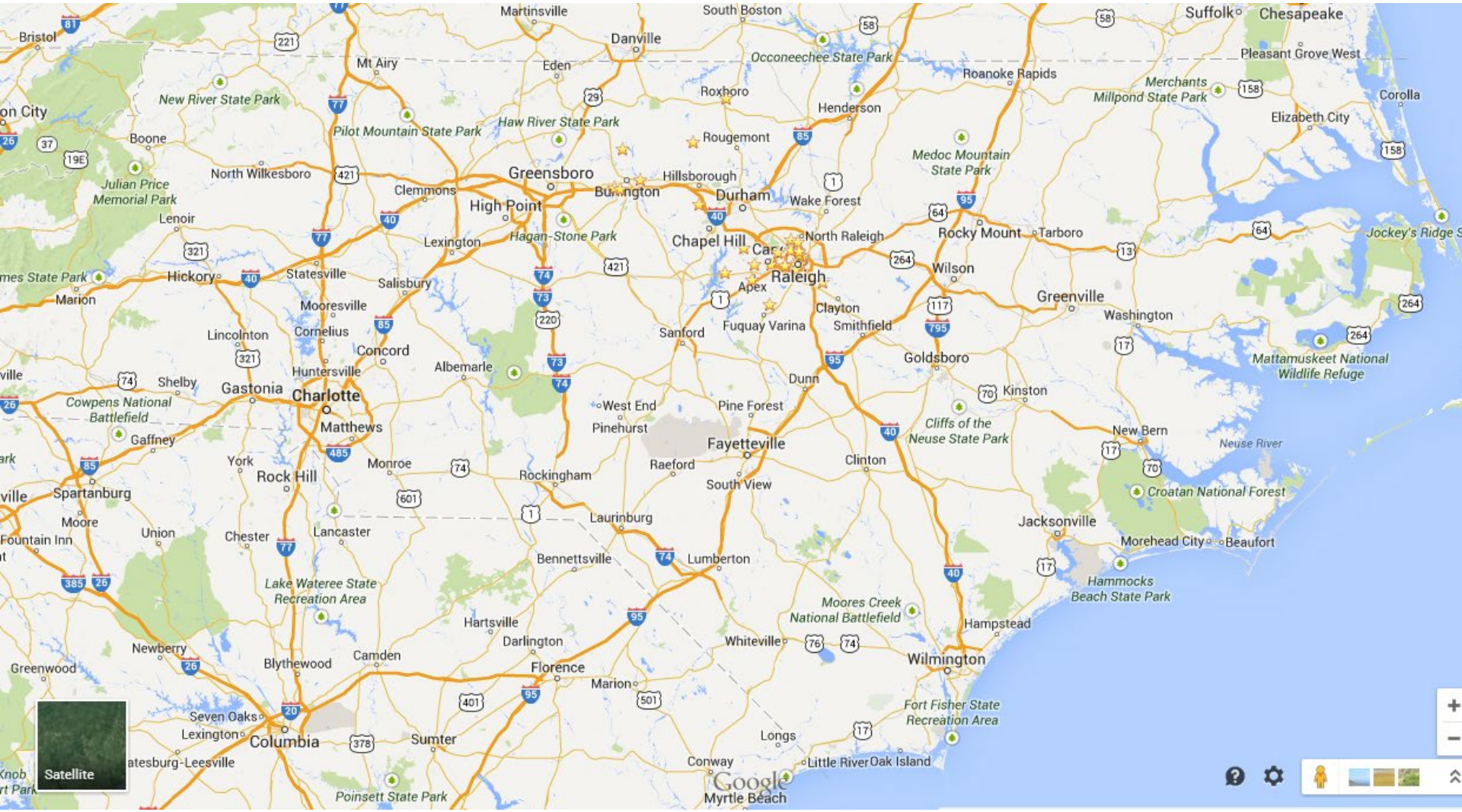
Trend in the EU for regulation of an increasing number of persistent organic pollutants in sewage sludge – 9 out 27 EU Countries (33%)
Regs on halogenated organics, phthalates, PCBs, dioxins, PAHs, LAS…

Specific POPs restrictions	Partial or complete restrictions for silviculture	Ban on use as agro fertilizer
Austria		
Belgium (Flanders)	Austria	
Belgium (Wallonia)	Belgium (Flanders)	
Denmark	France	*Netherlands (0.006%)
France	Germany	*Switzerland (not EU member)
Germany	Luxembourg	
Sweden	Netherlands	
Czech Republic		
Slovenia		

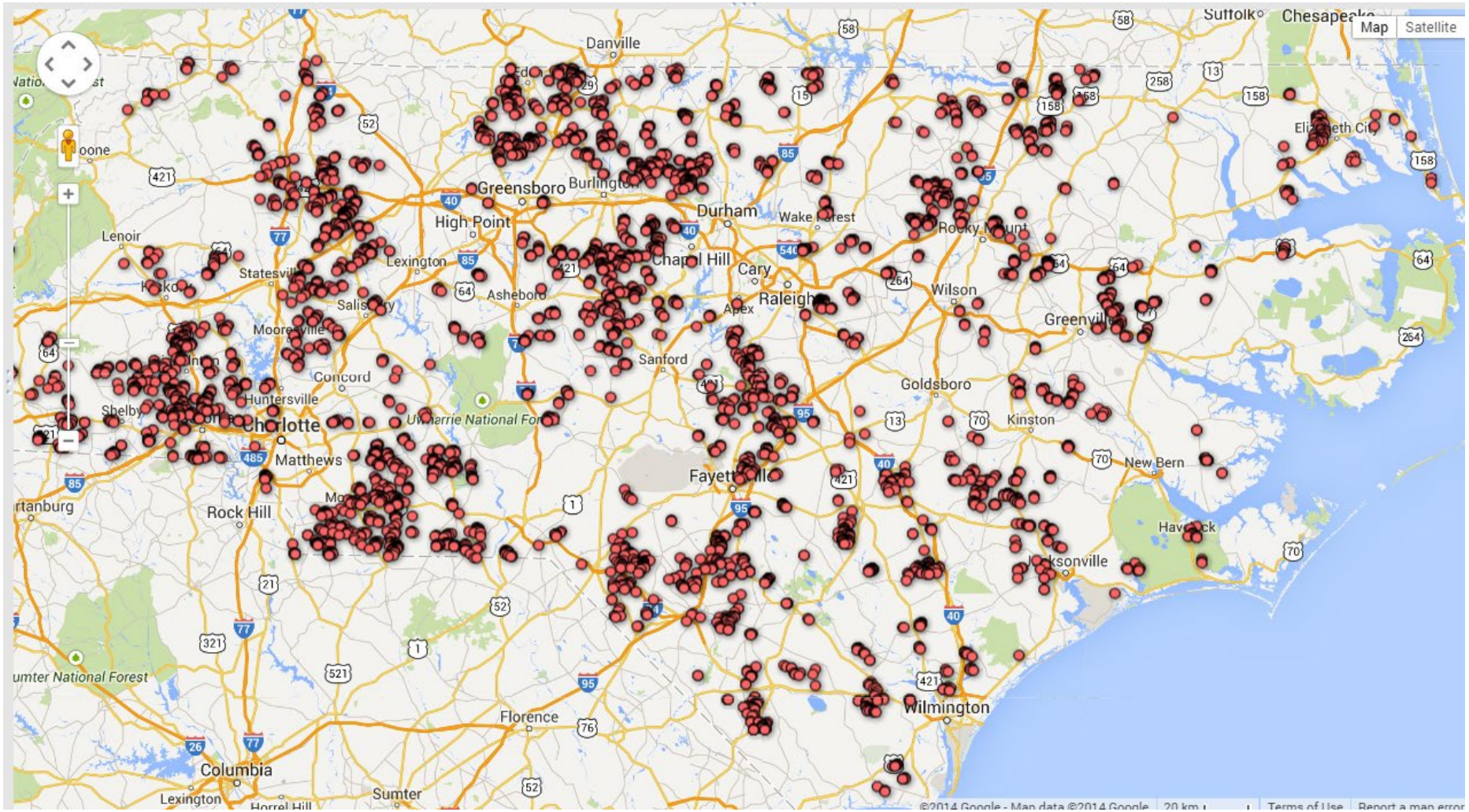
Kelessidis & Stasinakis, Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries, Waste Management 32 (2012) 1186–1195

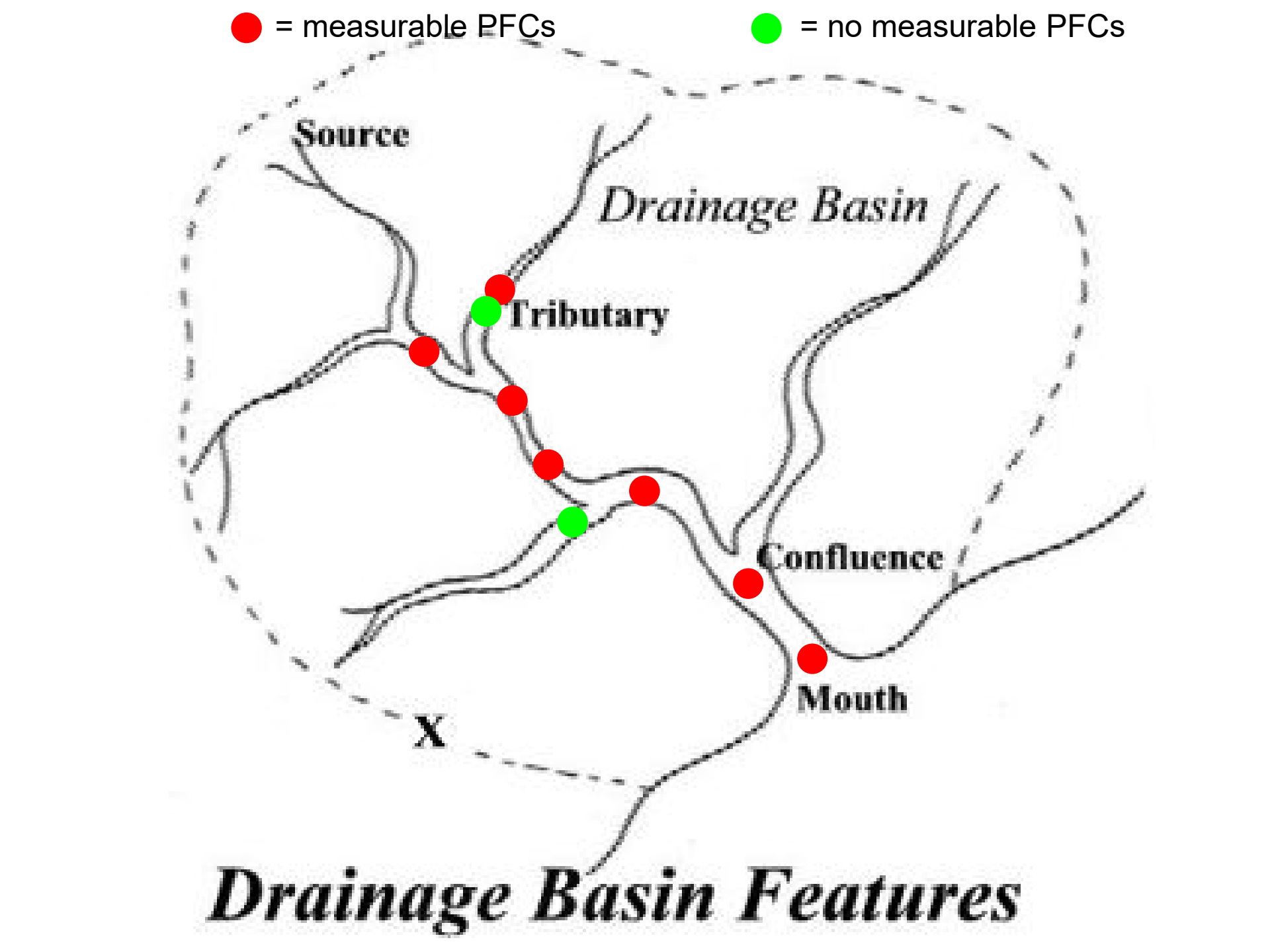
Also, more requirements e.g., heavy metals, other pathogens, applications

How do permitted land application sites influence surface water?

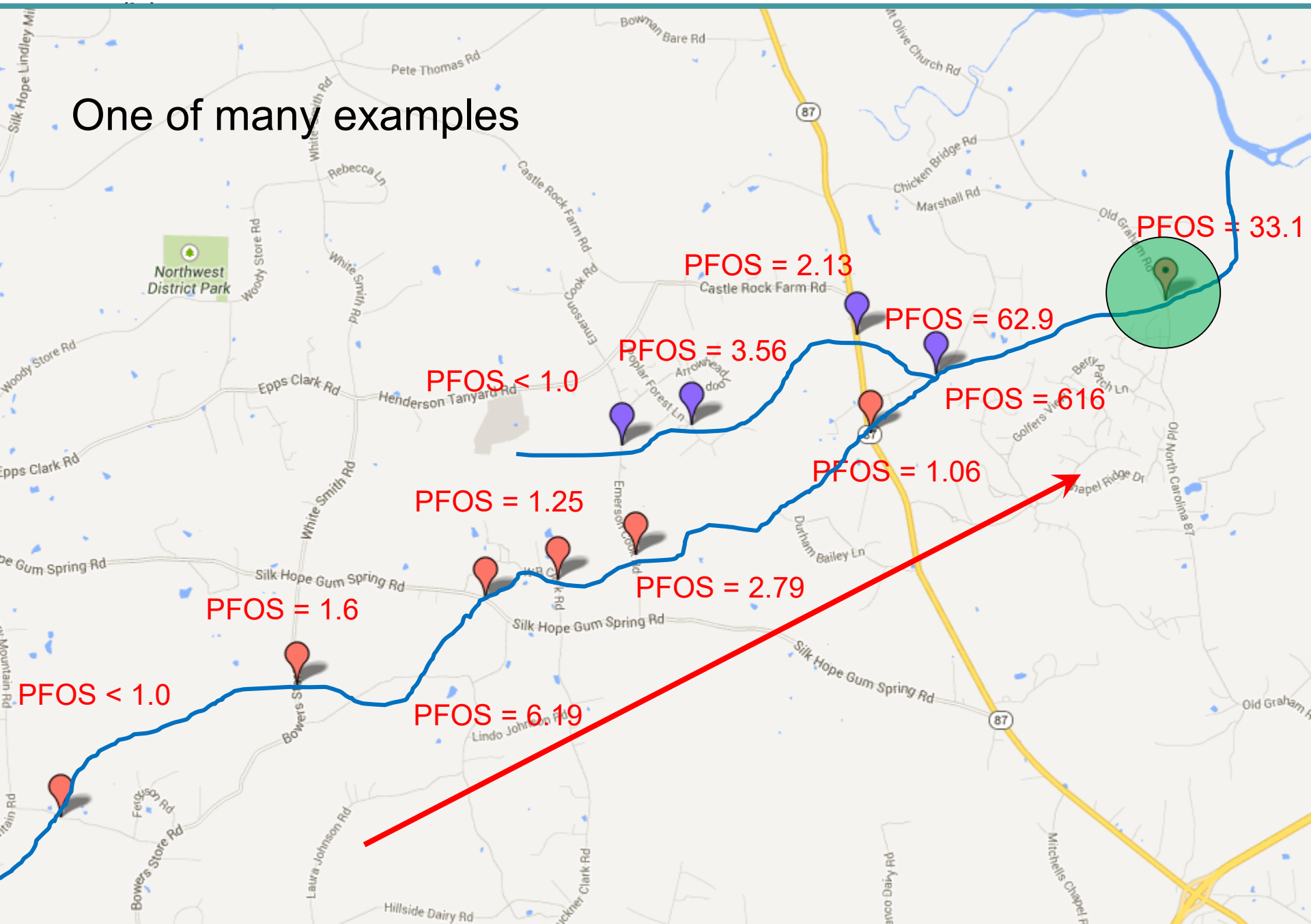


5,258 permitted sludge application sites in North Carolina




= measurable PFCs
= no measurable PFCs
Source
Drainage Basin
Tributary
Confluence
Mouth
X
Drainage Basin Features

Dry Creek Sub-basin (Initial recon results PFOS 154 ng/L PFOA 102

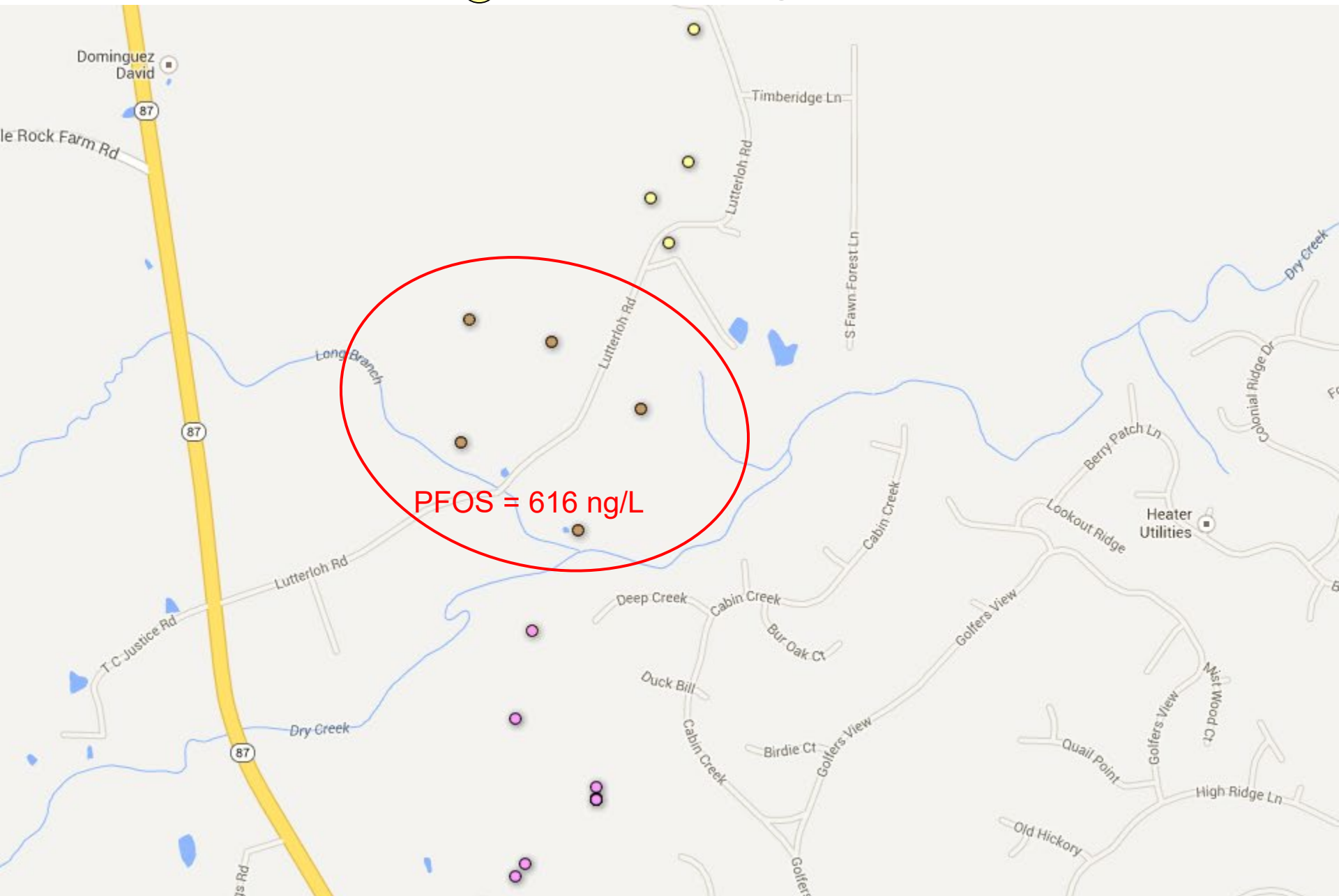


Dry Creek Subbasin (PFOS 154 ng/L PFOA 102 ng/L)

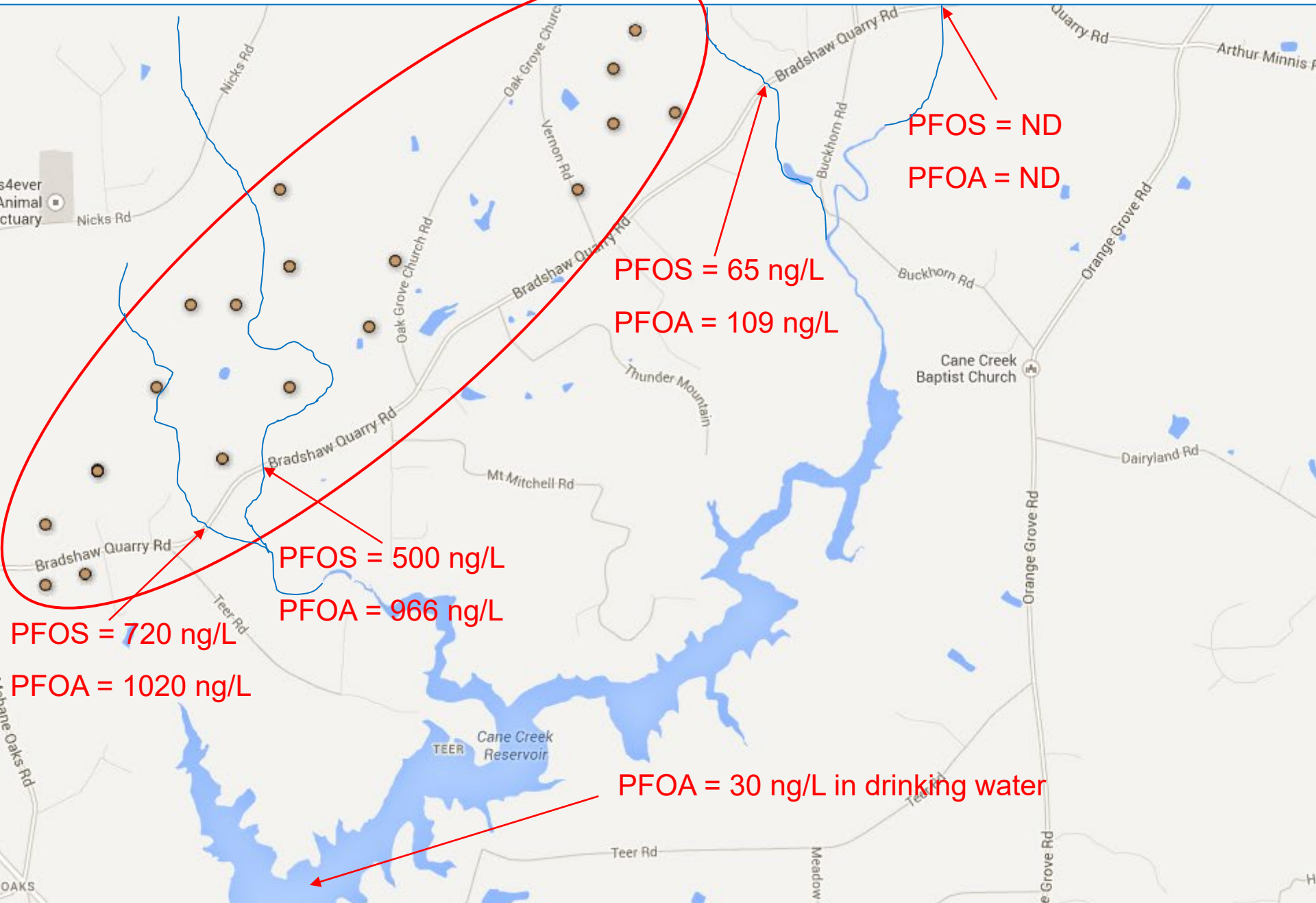

PFOS = 616 ng/L

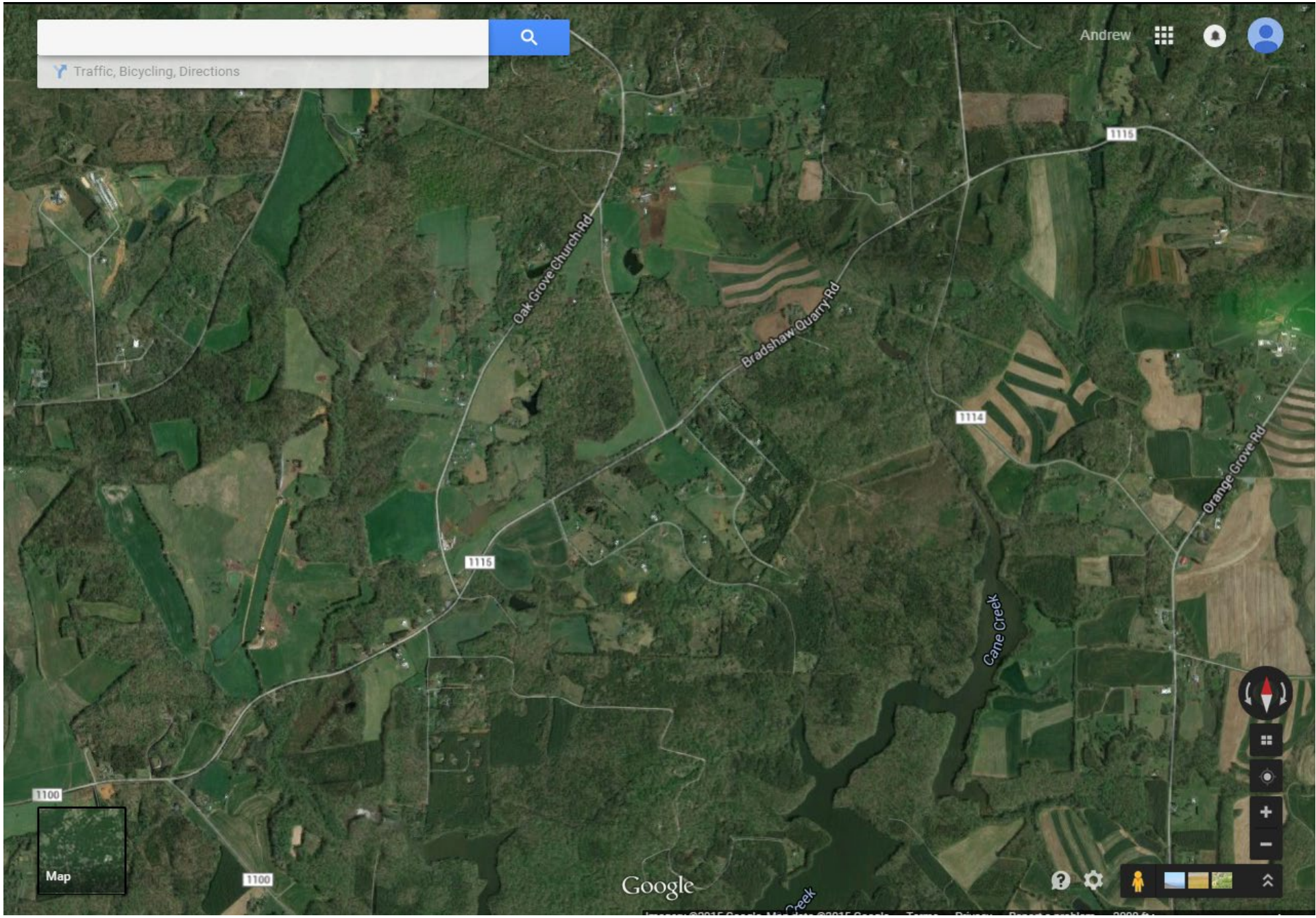
Permitted Sludge Application Sites in the Dry Creek Subbasin

= Municipal Utilities, = family residence, = reclaimed water



Sewage sludge in Cane Creek Resevoir basin - Serving Orange County, NC




Traffic, Bicycling, Directions
Andrew
Oak Grove Church Rd
Bradshaw Quarry Rd
1115
1114
1116
Orange Grove Rd
Cane Creek
1100
1100
Map
Google

Analysis of PFCs in local WWTP Sewage Sludge Supernatants (ng/L)

	South sludge 8/1	South sludge 8/1	East sludge 8/1	East sludge 8/1	South sludge 8/23	South sludge 8/23	East sludge 8/23	East sludge 8/23
C6	157	141	1080	1130	308	300	1280	1340
C7	210	191	880	883	384	446	1080	1300
PFHxS	203	214	734	738	478	459	1050	1010
PFBS	234	252	409	417	375	331	767	766
PFOA	179	177	648	705	535	565	1120	1130
C9	176	144	989	962	659	612	1170	1450
PFOS	284	216	1410	1300	1420	1170	1570	1680
C10	437	346	1830	1560	1810	1500	2180	2090
C5	100	100	159	167	72	64	331	289
C4	< 0	< 0	< 0	< 0	< 0	< 0	< 0	< 0
U2M3O-hex	< 0	< 0	< 0	< 0	< 0	< 0	< 0	< 0

Most compounds in the range 100s to 1000s ng/L in sludge supernatants applied to fields

Sewage sludge from these WWTPs is ~ 5% solid and 95% liquid supernatant

If PFOS has not been produced in the US in over a decade, why is it still present in sewage sludge?

Implications and Questions

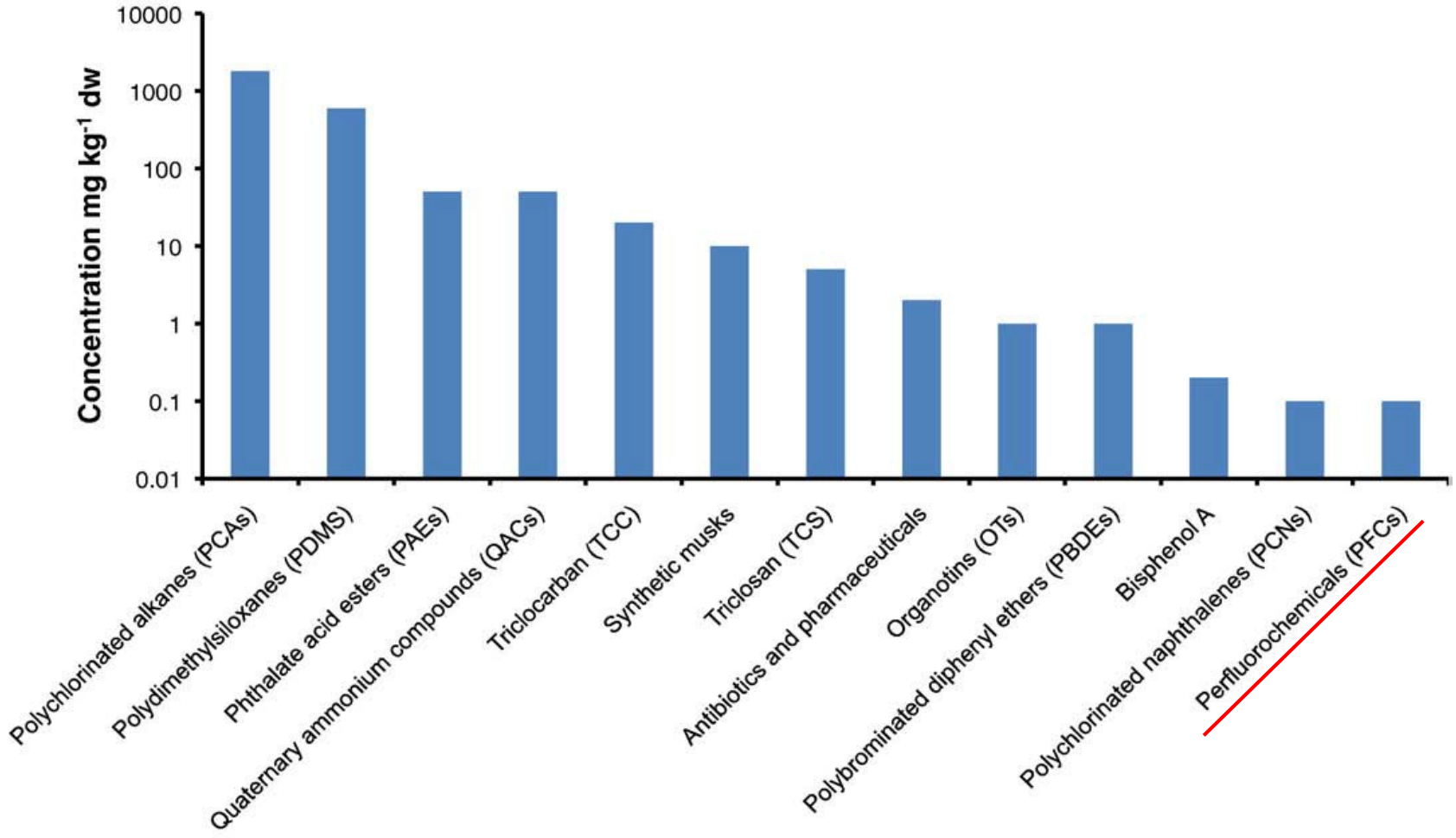
- Perfluorinated compounds at high concentrations in some sludges

- Surface application of these sludges leads to high concentrations of PFOS, PFOA, and related compounds in agricultural fields

- Persistence leads to contamination of agricultural crops and livestock, fisheries resources, surface water, drinking water, and the people living in these communities

- Sludge regulations in the U.S. only require testing for 9 metals and nutrients - other pollutants are not measured

Many other pollutants found in sewage sludge



Clarke & Smith (2011) Review of “emerging” organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids, *Environment International* (37) 226-247

Questions?

Email: lindstrom.andrew@epa.gov